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Studies of Solution. I.

The Change of Molecular Solution Volumes in Solutions.

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1. Introduction.

It is not recognizable that a solution would generally be formed by a simple physical mixture of solute and solvent. Solute and solvent, according to their relative properties, may form solutions in all possible proportions or in certain limited proportions. In the latter case, if there is an excess of solute, we obtain a purely physical mixture of a saturated solution and the solute. The fact of the existence of a saturated solution tells us that the constitution of a solution is something different from a simple physical mixture. Is, therefore, a solution a chemical compound? No, evidently not; because the composition of solution may be varied continuously within certain limits.

A solution which is neither a physical mixture nor a chemical compound, must, therefore, be formed by a kind of affinity between solute and solvent that is different both from chemical affinity and physical attractive force.

The term "physico-chemical affinity"[1] may be employed to designate this attractive force. The origin of these attractive forces may

1 L. Gruwitsch (Zs. physik. Chem., **87**, 333, (1914) and J. Russ. Phys. Chem. Soc., **47**, 805. (1915)) has studied the phenomena of partition and absorption in solution and explained the differences between three kinds of attractive forces, chemical, physical and physico-chemical.

perhaps be the same, and their differentiation may depend only upon the manner of their expressions; but, as physical attractive force and chemical affinity have been treated practically as quite different forces, so physico-chemical affinity may be treated as a special kind of attractive force. Physical attractive force is not of specific nature and it is expressed by a certain function of distance, but chemical affinity is very specific for substances and it is usually expressed by a comparatively simple function of the concentrations of components. At present, the definition and expression of physico-chemical affinity is not known, yet I think it an interesting method of study of solution to treat it as a problem of such an affinity.

In a study of solution from such a stand point, the usual chemical methods can not be employed and we are compelled to be content with the study of variation of certain physical properties of solution in accordance with the change of its composition.

As the physical properties of solution, viscosity, surface tension, specific gravity, optical properties, electric conductivity, heat capacity, vapour pressure, osmotic pressure, etc, have been studied by many chemists and physicists; most of these physical constants can not be determined separately by parts where solute and solvent play their rôles respectively. Thus there is no appropriate method for the study of solution but a discussion of the difference between the physical properties of real solution and those of the ideal solution which obeys the *admixture law*. Certain of these properties, however, such as electric conductivity and osmotic pressure, are favorable for our purpose as they depend upon only one component of a solution in lower concentrations, though in concentrated solutions, it is impossible to neglect the influence of the other component. Only one property, that is vapour pressure, may be separately determined as the partial pressures of solute and solvent; but the vapour phase is a kind of phase different from that of solution, therefore the conclusion[1] about the state of solution deduced from the studies of vapour pressures is indirect.

If there be a property which can separately be determined with respect to solute and solvent in the state of solution itself, there is confidence that the study of this property would make some important contribution to the knowledge of the nature of solution. As one such property, I have chosed the *molecular solution volumes* of solute

1 F. Dolezalek: Zs. physik. Chem., **64**, 727 (1908).

and solvent in solution. This is not perhaps the best for the present purpose; but I have no clue to any other which might better suit.

2. The Method of Determination of Molecular Solution Volumes of Solute and Solvent in Solution.

The change of volume in the formation of solution has been noticed from early times in the study of solution; and the fact that solution changes its volume according to temperature, pressure and concentration shows that the volume of a given substannce in solution is variable.

In order to discuss something about the volume of solute or solvent in solution, it is necessary to make the assumption that the total volume of a solution was made up as the sum of the two volumes which are occupied by the solute and solvent respectively. Taking into consideration the Richards' conception[1] of the compressible atoms or assuming that the free volume in solution is very small against its total volume, the above assumption is not non-plausible. The author designates such volumes as the "molecular solution volumes",[2] to distinguish them from the "molecular volume", as defined as (molecular weight)/(density).

Such molecular solution volumes of solute and solvent in solution have been seldom studied separately. Recently G. P. Baxter[3] studied the change of volume of solutions of alkali halides and tried to explain the complex phenomena by the theory of compressible atoms; but he did not turn his attention to the change of molecular solution

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1 *See* J. Amer. Chem. Soc., **36**, 2417 (1914).

2 J. Traube has first introduced the term molecular solution volume (*See* Smiles: The Relation between Chemical Constitution and some Physical Properties, p. 124.) If A_s is the molecular weight of a solute in grams, l the quantity of solvent which is present for every mol of solute, d the density of the solvent, d_s the density of the solution, the molecular solution volume of Traube is related to that of the solute of the author, φ_s, as follows:

$$\varphi_s = \frac{A_s + l}{d_s} - \frac{l}{d}.$$

In the present case, as the change of the volume of solvent is also taken into consideration, the second term of the above expression must be a function of the molecular solution volume of solvent such as $\varphi_s = \frac{A_s + l}{d_s} - \frac{l}{A_w}\varphi_w$ where φ_w and A_w are the molecular solution volume and the molecular weight of solvent respectively.

3 J. Amer. Chem. Soc., **33**, 922 (1911).

volumes of solute and solvent. Twelve years ago Carl Forch[1] attempted to determine the molecular solution volumes of solute and solvent in solution separately, but since his studies were limited to comparison of the molecular solution volumes of solutes in several kinds of solutions in a definite concentration, his work has drawn little attention and no one has continued the study of solution after such a manner. Forch's method however appears the only one whereby to determine the property of solution in separate parts with respect to solute and solvent.

Explanation of this method: If m_s mols of solute be present in one litre of solution of sp. gr. s, the mols of solvent m_w, in the solution is

$$m_w = \frac{1000s - m_s A_s}{A_w},$$

where A_s and A_w are the molecular weights of solute and solvent respectively.

If φ_s and φ_w be the molecular solution volumes of solute and solvent respectively, we have the following relation:

$$m_s\varphi_s + m_w\varphi_w = 1000.$$

The molecular solution volumes are of cause functions of concentration, say

$$\varphi_s = f_1(m_s, m_w) \qquad \text{and} \qquad \varphi_w = f_2(m_s, m_w),$$

but within the range where the change of concentration is not so large, we get the following two equations:

$$\left.\begin{aligned} m_{s_1}\varphi_s + m_{w_1}\varphi_w &= 1000 \\ m_{s_2}\varphi_s + m_{w_2}\varphi_w &= 1000 \end{aligned}\right\} \qquad (1)$$

From these equations we can calculate two unknown quantities φ_s and φ_w. That is, if we take two solutions which have known concentrations, we can calculate the molecular solution volumes of solute and solvent in the solution which has the mean concentration of the two solutions here chosen. To know the concentrations of the solute and solvent of a solution, we must determine the sp. gr. of the solution which has the known weight percentage of solute.

From equation (1)

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[1] Ann. Physik, [iv] **12.** 591 (1903). In the Forch's paper the term "molecular volume" of solute and solvent in solution is used, but not "molecular solution volume."

$$\left.\begin{aligned}\varphi_s &= \frac{1000(m_{w_1} - m_{w_2})}{m_{s_2}m_{w_1} - m_{s_1}m_{w_2}} \\ \varphi_w &= \frac{1000(m_{s_2} - m_{w_1})}{m_{s_2}m_{w_1} - m_{s_1}m_{w_2}}\end{aligned}\right\} \qquad (2)$$

Now, if the weight percentages of the solute in the two solutions chosen be denoted by a_1 and a_2, and the specific gravities of these solutions by s_1 and s_2 respectively, then

$$\varphi_s = \frac{1000[(100-a_1)s_1-(100-a_2)s_2]A_s}{[a_2(100-a_1)-a_1(100-a_2)]s_1s_2} pA_s. \qquad (3)$$

In the same way :

$$\varphi_w = \frac{1000[a_1s_1-a_2s_2]A_w}{[a_1(100-a_2)-a_2(100-a_1)]s_1s_2} = qA_w. \qquad (4)$$

As may be seen, the above equations (3) and (4) are independent to each other, with respect to their molecular weights, therefore the above method of calculation is also applicable to the determination of the molecular solution volumes of solute and solvent when the molecular weight of one of them is unknown. Moreover, if their molecular weights are both unknown, the relative volume change may be calculated in quite the same way. Therefore this method of calculation is also applicable to the case where the solute or solvent have ionized or polymerized in the solution.

In the present work, the change of molecular solution volumes in aqueous solutions of cane sugar and of alkali halides by the changes of temperature and concentration has been determined.

3. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Cane Sugar.

Plato[1] has determined very accurately the specific gravities of aqueous solutions of cane sugar. From his values, the data needed in the calculation of the molecular solution volumes were taken and the molecular solution volumes of cane sugar and water in the solutions have been calculated as shown in the following tables, where s denotes the specific gravity of solution and m_s and m_w the numbers of mols of cane sugar and water per litre and φ_s and φ_w the respective molecular solntion volumes.

1 Zs. Zuckerindustrie, **56**, 982. 1079, (1900); Landolt-Börnstein's Tabellen, p. 311.

TABLE 1.

0·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999868	0	55·500		
				204·7	18·019
5	1·02033	0·14909	53·801		
				206·6	18·015
10	1·04135	0·30433	52·020		
				208·4	18·004
20	1·08546	0·63447	48·200		
				209·9	17·986
30	1·13274	0·99314	44·012		
				211·3	17·968
40	1·18349	1·38347	39·415		
				213·0	17·891
50	1·23775	1·80865	34·352		
				214·7	17·804
60	1·29560	2·27181	28·765		
				216·1	17·700
70	1·35719	2·77645	22·600		
60	1·29560	2·27181	28·765		
				215·8	17·719
65	1·32591	2·51871	25·759		
				216·4	17·665
70	1·35719	2·77645	22·600		

TABLE 2.

10·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999727	0	55·491		
				208·9	18·021
5	1·01960	0·14899	53·765		
				209·6	18·019
10	1·04016	0·30400	51·962		
				210·5	18·018
20	1·08353	0·63333	48·114		
				211·6	17·998
30	1·13014	0·99085	43·911		
				212·9	17·970
40	1·18020	1·37964	39·305		
				214·3	17·920
50	1·23382	1·80286	34·242		
				215·8	17·844
60	1·29117	2·26404	28·667		
				217·1	17·737
70	1·35230	2·76644	22·518		
60	1·29117	2·26404	28·667		
				216·7	17·767
65	1·32125	2·50986	25·668		
				217·4	17·701
70	1·35230	2·76644	22·518		

TABLE 3.

20·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·998230	0	55·408		
				210·7	18·048
5	1·01784	0·14873	53·671		
				211·3	18·047
10	1·03813	0·30339	51·860		
				212·0	18·042
20	1·08094	0·63180	47·999		
				213·1	18·029
30	1·12698	0·98806	43·789		
				214·2	18·004
40	1·17648	1·37529	39·180		
				215·5	17·959
60	1·22958	1·79671	34·124		
				216·8	17·890
60	1·28644	2·25575	28·562		
				218·0	17·790
70	1·34716	2·75594	22·432		
50	1·28644	2·25575	28·562		
				217·7	17·818
65	1·31631	2·50047	25·572		
				218·3	17·760
70	1·34716	2·75594	22·432		

TABLE 4.

30·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·995673	0	55·266		
				211·7	18·094
5	1·01518	0 14834	53·530		
				212·4	18·092
10	1·03530	0·30257	51·719		
				213·5	18·087
20	1·07767	0·62990	47·854		
				214·4	18·074
30	1·12324	0·98479	43·643		
				215·7	18·045
40	1·17214	1·37018	39·036		
				216·4	18·018
50	1·22495	1·78982	33·996		
				217·8	17·955
60	1·28144	2·24699	28·451		
				219·0	17·855
70	1·34181	2·74499	22·348		
60	1·28144	2·24699	28·451		
				218·7	17·883
65	1·31113	2·49063	25·471		
				219·3	17·823
70	1·34181	2·74499	22·343		

TABLE 5

40·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·992241	0	55·076		
				212·1	18·157
5	1·01169	0·14781	53·348		
				213·9	18·151
10	1·03165	0·30150	51·537		
				214·9	18·145
20	1·07366	0·62755	47·676		
				215·7	18·132
30	1·11888	0·98096	43·473		
				216·5	18·113
40	1·16759	1·36462	38·885		
				217·6	18·092
50	1·21996	1·78265	33·857		
				218·7	18·019
60	1·27615	2·23771	28·333		
				219·9	17·927
70	1·33625	2·73362	22·250		
69	1·27615	2·23771	28·333		
				219·6	17·953
65	1·30571	2·48034	25·366		
				220·2	17·895
70	1·33625	2·73362	22·250		

TABLE 6.

50·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·98807	0	55·844		
				213·7	18·233
5	1·00735	0·14720	53·118		
				214·9	18·229
10	1·02720	0·30020	51·314		
				215·9	18 224
20	1·06898	0·62481	47·468		
				216·6	18·215
30	1·11398	0·97668	43·283		
				217·5	18·196
40	1·16248	1·35893	38·714		
				218·5	18·160
50	1·21465	1·77489	33·710		
				219·7	18·096
60	1·27058	2·22794	28·210		
				220·8	18·008
70	1·33047	2·72179	22·155		
60	1·27058	2·22794	28·210		
				220·5	18·031
65	1·30002	2·46952	25·256		
				221·0	17·980
70	1·33047	2·72179	22·155		

TABLE 7.

60·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·98330	0	54·579		
5	1·00231	0·14646	52·853	251·96	18·322
10	1·02198	0·29868	51·054	216·5	18·320
20	1·06358	0·62164	47·226	217·1	18·317
30	1·10850	0·97190	43·070	217·3	18·314
40	1·15693	1·35244	38·530	218·2	18·293
50	1·20891	1·76650	33·551	219·5	18·250
60	1·26468	2·21760	28·079	220·6	18·190
70	1·32447	2·70951	22·055	221·7	18·104
60	1·26468	2·21760	28·079		
65	1·29408	2·45825	25·140	221·5	18·125
70	1·32447	2·70951	22·055	221·9	18·078

In the above tables, since the calculation of the molecular solution volumes was performed with data for one pair of solutions, they represent the molecular solution volumes for the solution of the mean concentration of the two which are chosen for the calculation.

In the above tables, for the molecular solution volumes of cane sugar, the calculations were carried out to four figures; and for those of water to five figures, taking the molecular weights[1] of cane sugar and water as 342·176 and 18·016 respectively. Such calculation may appear unreasonable, because the molecular weights used were not accurate in the third desimal figure; in the present case, however, the absolute values of molecular solution volumes are not needed but relative ones and therefore if a definite value be taken for the molecular weight, we could get accurate *relative* values of the molecular solution volumes.

When the solute is an easily weighable substance, we can determine the quite accurate value of weight percentage of the solute in the solution. In such a case, the accuracy of the calculated value of the molecular solution volume depends only on that of the specific gravity of the solution, and consequently the greatest error of φ_s and φ_w de-

1 According to the international atomic weights for 1916, the molecular weight of cane sugar is 342·236, but this slight difference in the moleculur weight does not bring any appreciable effect on the values of molecular solution volumes.

pends on the terms $(100-a_1)s_1-(100-a_2)s_2$ and $s_1a_1-s_2a_2$ respectively as seen in the equations (3) and (4).

4. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Alkali Halides.

The following four salts were taken: potassium chloride, sodium chloride, ammonium chloride and lithium chloride. As the materials, Merk's preparations of potassium chloride and ammonium chloride were used, after recrystallization; sodium chloride was purified by precipitation with hydrochloric acid gas from the solution; and lithium chloride was prepared in the following way: Commercial lithium chloride, after recrystallization, was fused in a platinum dish and then dissolved in water and again recrystallized. Lithium chloride is very hygroscopic and moreover it crystallizes with one or two molecules of water of crystallization[1] at room temperatures; therefore it is very difficult to weigh out a definite quantity of it, but it is more definite when fused. To avoid its decomposition, the fusion was accomplished in a combustion tube in a current of dry hydrochloric acid gas, according to Baxter[2]. For the preparation of a concentrated solution, a great quantity of the salt was required and in that case a platinum crucible was taken to the fusion. The crucible was set on a hollow on an asbestus plate and covered with a large inverted funnel through which a current of hydrochloric acid gas was conducted. By gentle heating of the crucible from the bottom, a fused salt was obtained which contained no trace of free alkali; but the cooling of the fused mass had to be very carefully conducted, lest a small quantity of lithium chloride should be decomposed, forming difficultly soluble lithium oxides. The fused salt thus formed could easily be detached from the crucible and it was quickly transferred into a tared weighing tube and, after cooling in a desiccator was weighed. As solvent water a conductivity water from which any dissolved gas was removed by boiling, was used.

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[1] The transition temperature of hydrated lithium chlorides, $LiCl.2H_2O$ and $LiCl.H_2O$, is given as 26° or 15·9°C. in Abegg's Handbuch der anorganischen Chemie and Landolt-Börnstein's Tabellen respectively. By the determination of the author, the minimum values of the specific gravities of lithium chloride solutions (3%–40%) were always near 23°C, and this may be perhaps the transition temperature.

[2] *Loc. cit.*

The preparation of solutions: in the case of potassium chloride and ammonium chloride, a solution of a definite weight percentage was prepared by weighing water at first and then dissolving the calculated amount of salt in it. For the correction against the bouyancy in air, the specific gravities of potassium chloride and sodium chloride were taken as 2·00 and 2·14 after Baxter[1], but as to ammonium chloride the literature gives several values and as any great accuracy was not required here, the value 1·52 was adopted. In the case of lithium chloride, as a definite amount of the salt could not be weighed out, the order of procedure was reversed; namely a calculated amount of water was added to a definite amount of salt. In this case the solution had to be weighed directly and the necessary data for the correction against the bouyancy in air were taken from those given by Gerlach[2]. In the preparation of a definite solution of lithium chloride, two solutions were prepared independent of each other and when the difference of specific gravities do not exceed 1/20000, it was assumed that the solutions had the correct percentage.

The method of determination of specific gravity: An Ostwald-Sprenger's pyknometer whose capacity is ca. 20 cc., was used. For the determination of specific gravities at several temperatures, it would have been convenient to use the dilatometric method, but in accuracy that is far inferior to the direct method. The pyknometer method was mostly used and in some cases the pyknometer itself was used as a dilatometer, one of the capillary limbs being calibrated.

For the thermostat of ordinary or higher temperature a toluene gas regulator was used; but for that below the room temperature an electric toluence regulator was used. A 2 volts current was used as the first circuit, shut or opened by a toluene regulator. By the aid of a small relay, this first current was used to shut or open a second circuit of 40 volts which, by the aid of a larger relay, shut or opened an ice water current to the thermostat. In this manner the temperature of the thermostat was automatically regulated to within 0·1°C.

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1 *Loc. cit.*

2 Zs. analy. Chem., 8, 281 (1869).

I. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Potassium Chloride.

TABLE 8.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	40°	50°
0	0·999868	0·999727	0·99823	0·995673	0·992241	0·98807
5	1·03369	1·03262	1·02976	1·02728	1·02341	1·01912
10	1·06799	1·06605	1·06272	1·05975	1·05572	1.05108
15	1·10304	1·10039	1·09657	1·09331	1·08891	1·08410
20	1·13930	1·13615	1·13186	1·12826	1·12367	1·11877
25	—	1·17317	1·16835	1·16470	1·15999	1·15484
29	—	—	—	1·17970	1·17482	1·16969

TABLE 9.

0·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999868	0	55·499		
5	1·03369	0·693818	54·506	25·81	18·019
10	1·06799	1·4324	53·352	28·08	17·989
15	1·10304	2·2191	52·041	29·89	17·941
20	1·13930	3·0561	50·591	31·00	17·894

TABLE 10.

10·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999727	0	55·491		
5	1·03262	0·69218	54·450	27·10	18·021
10	1·06605	2·4298	53·255	29·16	17·995
15	1·10039	2·2137	51·917	30·66	17·954
20	1·13615	3·0476	50·451	31·51	17·918
30	1·17317	3·9336	43·838	32·51	17·85

TABLE 11.

20·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·998230	0	55·408		
5	1·02976	0·69056	54·300	28·95	18·048
10	1·06272	1·4253	53·089	29·74	18·038
15	1·09657	2·2061	51·736	31·17	18·000
20	1·13186	3·0361	50·260	31·96	17·966
25	1·16855	3·9181	78·646	32·79	17·92

TABLE 12.

30·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·995673	0	55·266		
5	1·02728	0·68889	54·168	28·85	18·094
10	1·05975	1·4214	52·941	30·28	18·077
15	1·09331	2·1995	51·583	31·51	18·043
20	1·12826	3·0254	50·100	32·30	18·008
25	1·16470	3·9053	48·487	33·26	17·95
27	1·17970	4·2713	47·800	33·53	17·93

TABLE 13.

40·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·992241	0	55·076		
5	1·02341	0·6863	53·965	29·39	18·157
10	1·05572	1·4159	52·739	30·49	18·143
15	1·08891	2·1907	51·376	31·78	18·109
20	1·12367	3·0141	49·897	32·48	18·079
25	1·15999	3·8891	48·286	33·21	18·03
27	1·17482	4·2542	47·602	33·71	18·00

TABLE 14.

50·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·98807	0	54·844		
5	1·01912	0·6834	53·737	29·52	18·233
10	1·05108	1·4097	52·507	31·15	18·226
15	1·08410	2·1810	51·149	32·01	18·185
20	1·11877	3·0009	49·679	32·56	18·163
25	1·15484	3·8721	48·075	33·33	18·11
27	1·16969	4·2621	47·394	33·90	18·07

II. The Malecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Sodium Chloride.

TABLE 15.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	40°	50°
0	0·999868	0·999727	0·99823	0·995673	0·992241	0·98807
5	1·03802	1·03656	1·03398	1·03071	1·02666	1·02210
10	1·07659	1·07394	1·07051	1·06664	1·06223	1·05729
15	1·11606	1·11235	1·10825	1·10386	1·09902	1·09381
20	1·15635	1·15206	1·14742	1·14258	1·13743	1·13198
23	1·18104	1·17634	1·17145	1·16632	1·16099	1·15551
26	1·20652	1·20151	1·19633	1·19099	1·18546	1·17980

TABLE 16.

0·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999868	0	55·499		
5	1·03802	0·88782	54·735	15·51	18·019
10	1·07659	1·8415	53·781	17·98	17·979
15	1·11601	2·8630	52·649	19·86	17·915
20	1·15635	3·9559	51·347	21·23	17·840
23	1·18104	4·6467	50·478	22·33	17·755
27	1·20652	5·3659	59·557	22·69	17·723

TABLE 17.

10·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999727	0	55·491		
5	1·03656	0·88654	54·657	16·95	18·021
10	1·07394	1·8370	53·648	19·08	17·988
15	1·11235	2·8541	52·481	22·58	17·935
20	1·15206	3·9419	51·157	21·76	17·871
23	1·17634	4·6281	50·276	22·82	17·82
26	1·20151	5·3435	49·351	22·98	17·77

TABLE 18.

20·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·99823	0	55·408		
5	1·03393	0·88429	54·519	18·14	18·048
10	1·07051	1·8311	53·476	19·83	18·022
15	1·10825	2·8433	52·284	21·52	17·955
20	1·14742	3·9254	50·950	22·09	17·925
23	1·17145	4·6088	50·067	23·05	17·850
26	1·19633	5·3206	49·136	23·27	17·831

TABLE 19.

30·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·995673	0	55·266		
5	1·03071	0·88156	54·350	18·80	18·094
10	1·06664	1·8246	53·284	20·43	18·067
15	1·10386	2·8324	52·081	21·52	18·030
20	1·14258	3·9085	50·736	22·46	17·979
23	1·16632	4·5887	49·848	23·39	17·91
26	1·19099	5·2969	48·919	23·48	17·89

TABLE 20.

40·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·992241	0	55·076		
5	1·02666	0·8781	54·137	19·42	18·157
10	1·06233	1·8170	53·063	20·75	18·135
15	1·09902	2·8200	51·852	21·85	18·097
20	1·13743	3·8913	50·507	22·67	18·053
23	1·16099	4·5677	49·620	23·58	17·98
26	1·18546	5·2722	48·692	23·68	17·97

TABLE 21.

50·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·98807	0	54·844	19·82	18·232
5	1·02210	0·8742	53·895	21·05	18·212
10	1·05729	1·8085	52·815	22·06	18·178
15	1·09381	2·8065	51·606	22·82	18·137
20	1·13198	3·8726	50·265	23·71	18·07
23	1·15551	4·5458	49·382	23·75	18·07
26	1·17980	5·2471	48·460		

III. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Ammonium Chloride.

TABLE 22.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	49°	50°
0	0·99987	0·999727	0·99823	0·995673	0·992241	0·98807
5	1·01672	1·01573	1·01377	1·01086	1·00731	1·00326
10	1·03250	1·03084	1·02840	1·02536	1·02170	1·01767
15	1·04763	1·04441	1·04264	1·03929	1·03558	1·03157
20	1·06220	1·05951	1·05642	1·05302	1·04919	1·04516
25	—	—	1·06997	1·06638	1·6250	1·05845
30	—	—	—	—	1·07584	1·07172

TABLE 23.

0·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·99987	0	55·499	35·81	18·019
5	1·01672	0·9346	53·611	37·82	18·012
10	1·03250	1·9299	51·579	38·32	17·96
15	1·04763	2·9373	49·428	39·16	17·91
20	1·06220	3·9708	47·167		

TABLE 24.
10·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·999727	0	55·491		
				36·66	18·021
5	1·01573	0·9493	53·560		
				38·22	17·988
10	1·03084	1·9268	51·496		
				38·88	17·95
15	1·04441	2·9310	49·323		
				39·59	17·93
20	1·05951	3·9608	47·048		

TABLE 25.
20·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	9·998230	0	55·408		
				37·18	18·048
5	1·01377	0·9475	53·456		
				38·50	18·025
10	1·02840	1·9223	51·374		
				39·23	17·99
15	1·04264	2·9233	49·192		
				39·94	17·97
20	1·05642	3·9492	46·910		
				40·38	17·92
25	1·06997	4·9999	44·542		

TABLE 26.
30·0°C.

%	s	m_s	m_w	φ_s	ψ_w
0	0·995673	0	55·266		
				37·69	18·094
5	1·01086	0·94473	53·303		
				38·69	18·075
10	1·02536	1·9166	51·222		
				39·59	18·040
15	1·03929	2·9139	49·034		
				40·05	18·01
20	1·05302	3·9366	46·760		
				40·62	17·96
25	1·06638	4·9831	44·393		

TABLE 27.
40·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·992241	0	55·076		
				37·83	18·157
5	1·00731	0·94141	53·115		
				38·90	18·137
10	1·02170	1·9097	51·039		
				39·75	18·108
15	1·03558	2·9035	48·858		
				40·25	18·07
20	1·04919	3·9222	46·589		
				40·79	18·03
25	1·06250	4·9650	44·231		
				40·98	18·00
30	1·07584	6·0328	41·801		

TABLE 28.

50·0°C.

%	s	m_s	m_w	φ_s	φ_w
0	0·98807	0	54·844		
5	1·00326	0·93763	52·902	37·79	18·231
10	1·01767	1·9022	50·839	38·95	18·213
15	1·03157	2·8923	48·670	39·83	18·177
20	1·04516	3·9072	46.410	40·41	18·14
25	1·05845	4·9461	44·127	40·89	18·09
30	1·07172	6·0097	41·545	41·16	18·07

IV. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Lithium Chloride.

TABLE 29.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	40°	50°
0	0·996868	0·999727	0·998230	0·995673	0·992241	0.98807
3	(1·0185)*	1·0178	1·0176	1·0175	1.0176	1·0177
6	(1·0357)*	1·0351	1·0349	1·0347	1·0348	1·0350
10	1.0598	1·0584	1·0579	1·0577	1·0554	1·0584
20	1·1199	1·1178	1·1170	1·1169	1·1174	1·1185
30	1·1860	1·1833	1·1823	1·1821	1·1828	1·1843
35	1·2218	1·2176	1·2189	1·2175	1·2180	1·2197
40	1·2601	1·2568	1·2554	1·2551	1·2556	1·2573

TABLE 30.

10·0C°.

%	s	m_s	m_w	φ_s	φ_w
0	0·99973	0	55·491		
3	1·0178	0·72016	54·800	17·30	18·021
6	1·0351	1·4647	54·006	19·19	17·996
10	1·0584	2·4963	52·875	19·71	18·001
20	1·1178	5·2726	49·637	21·04	17·93
30	1·1833	8·3720	45·975	21·15	17·90
35	1·2189	1·0063	43·976	21·17	17·89
40	1·2568	1·1857	41·855	21·15	17·89

* The values were obtained by extrapolation.

0	0·99973	0	5·5491	18·27	18·021
6	1·0351	1·4647	5·4006		

TABLE 31.

30·0°C.

%	s	m_s	m_w	φ_s	ψ_w
0	0·995673	0	55·266	12·08	18·094
3	1·0175	0·71996	54·785	19·26	18·000
6	1·0347	1·4642	53·989	20·05	17·979
10	1·0577	2·4646	52·840	20·97	17·94
20	1·1167	5·2686	49·597	21·17	17·92
30	1·1821	8·3540	45·931	21·28	17·89
35	1·2175	1·0050	43·925	21·28	17·89
40	1·7551	1·1840	41·797		
0	0·995673	0	55·266	15·78	18·094
6	1·0347	1·4642	53·989		

TABLE 32.

50·0°C.

%	s	m_s	m_m	φ_s	ψ_w
0	0·98807	0	54·844	12·4	18·232
3	1·0177	0·72006	54·795	19·12	17·999
6	1·0350	1·4646	54·004	19·72	17·983
10	1·0584	2·4963	52·873	20·68	17·94
20	1·1185	5·2760	49·667	21·06	17·89
30	1·1843	8·3793	46·015	21·27	17·86
35	1·2197	10·068	44·004	21·23	17·86
40	1·2573	11·861	41·872		
0	0·98807	0	54·844	10·5	18·202
6	1·0350	1·4646	54·004		

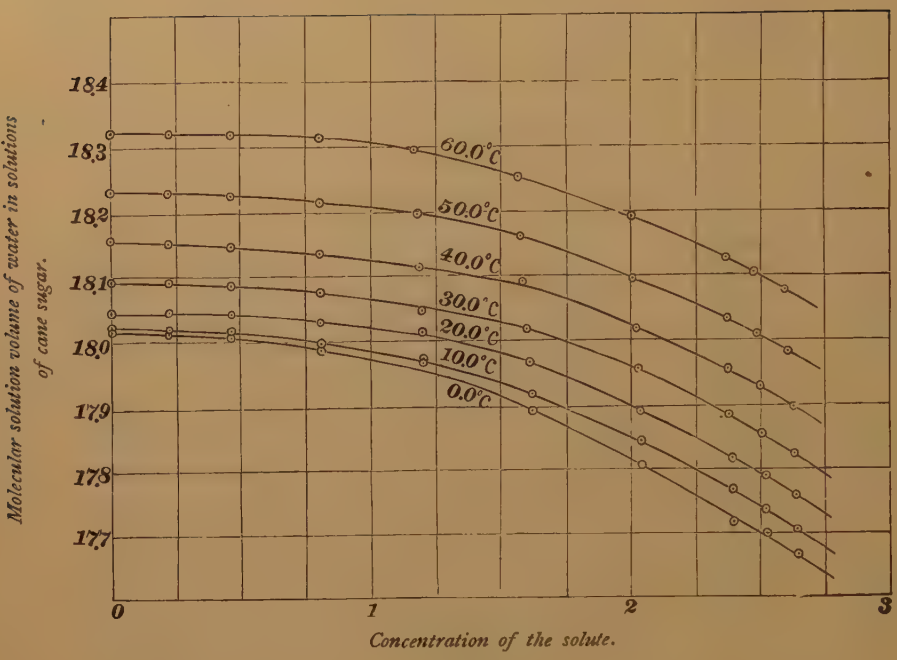


Fig. 1.

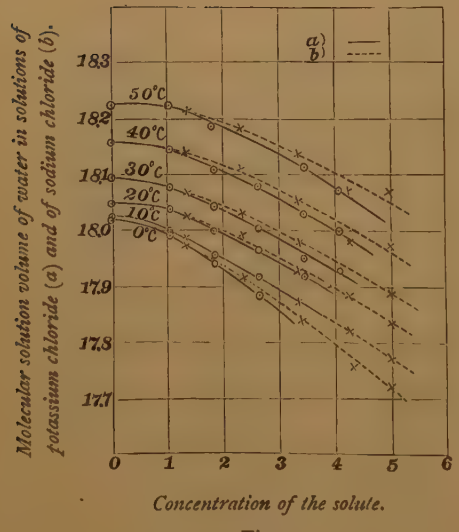


Fig. 2.

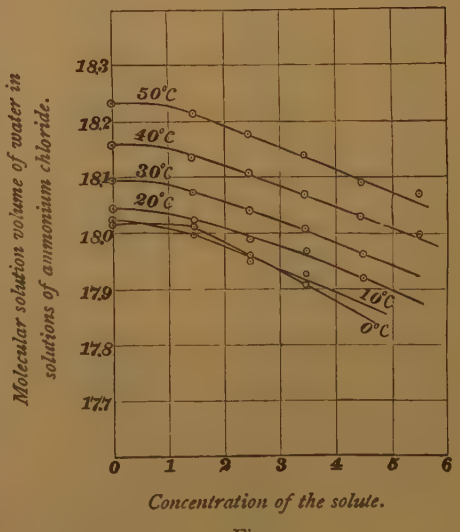


Fig. 3.

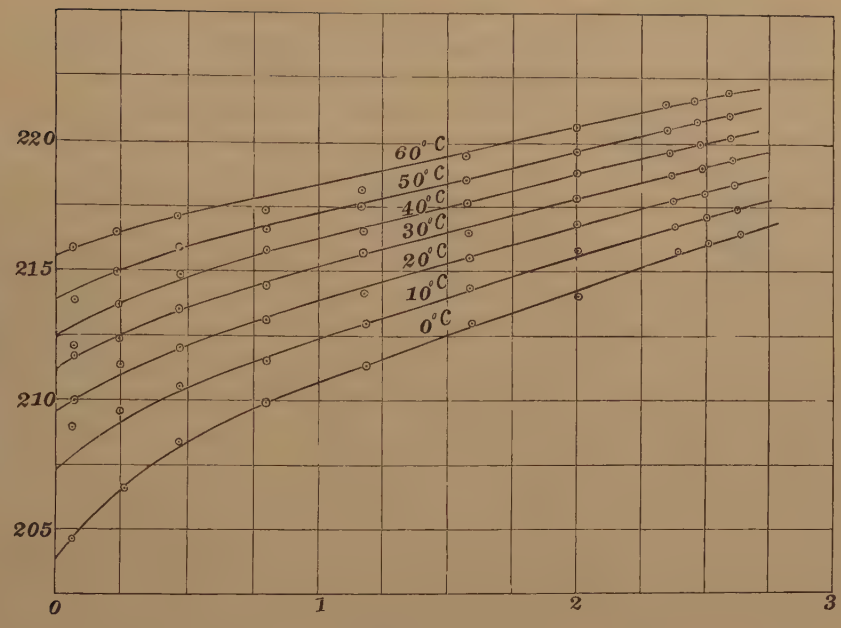


Fig. 4.

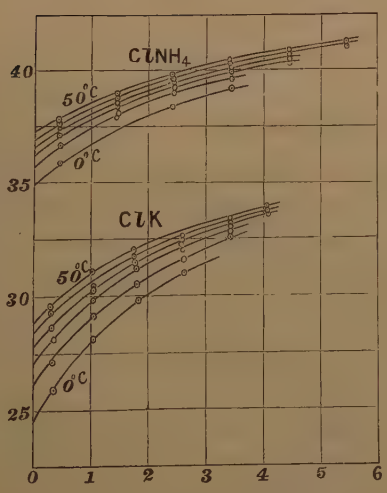


Fig. 5.

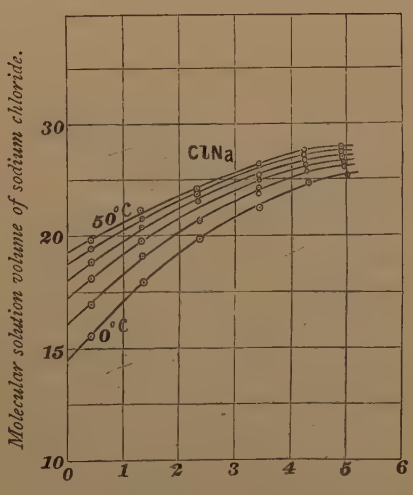


Fig. 6.

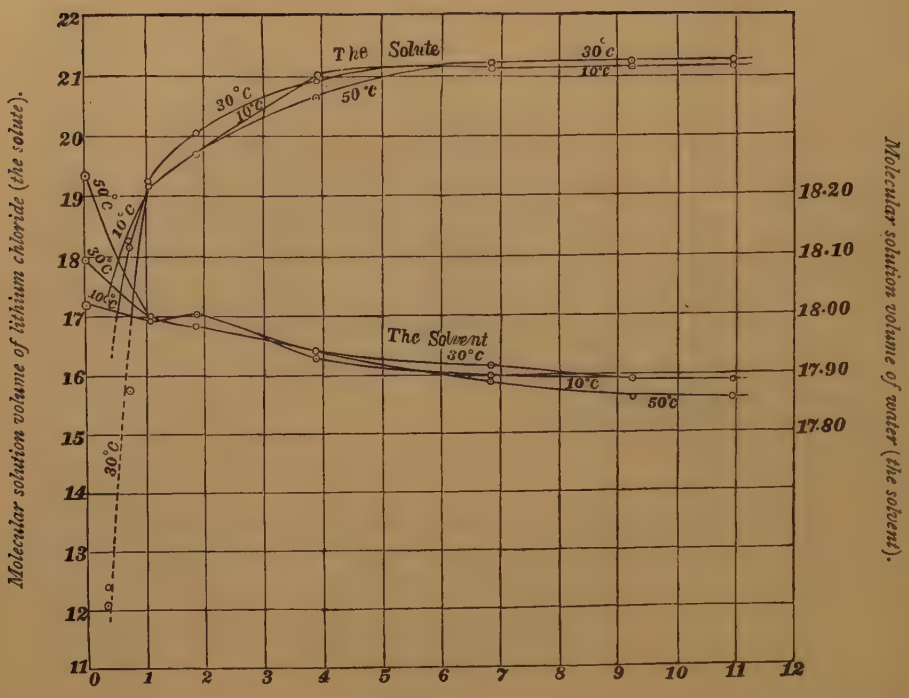


Fig. 7.

5. Discussion of the Results.

Representing graphically the above results, taking the molecular solution volume as ordinates and the number of mols of solute in one litre of solution as abscissa, Figg. 1–7 were obtained. As seen from these figures, the volume change of solution is the total sum of the volume changes of the solute and solvent; and, in general, the volume of solvent contracted by an increase of the concentration of the solute, while the volume of solute dilated.

The volume of the solvent in solution. As seen from Figg. 1–3, in all the solutions above examined, except those of lithium chloride, the molecular solution volume-concentration curves for the solvent are of the same form. So far as the concentration of solute is lower than one mol per litre, the contraction of solvent is very small, but in higher concentrations it becomes greater until at last it becomes a linear function of the concentration.

Now, the cause of the change of volume in solution appears to depend on the molecular cohesion or physico-chemical affinity between solute and solvent. If the solution is dilute the sphere of action of solute molecules does not extend to all the solvent molecules in the solution, and the greater part of solvent molecules, which are not affected by solute molecules, would be in the same state of aggregation as in the pure state; thus the change of volume of solvent in dilute solutions is very small. In more concentreted solutions, however, the sphere of action of solute extends to all the solvent molecules, and the volume of solvent whould change linearly with the concentration of the solute.

The amount of volume change of solvent, as above described, is seen to be one of the measures of the physico-chemical affinity between solute and solvent. The following table represents the amount of volume contraction which takes place when the concentration varies from 1·5 molars to 2·5.

TABLE 33.

Compressibility of the Solvent (Water).

	0°C.		10°C.		20°C.	
	in cc.	%	in cc.	%	in cc.	%
$C_{12}H_{22}O_{11}$	0·20	1·11	0·19	1·05	0·18	1·0
ClK	0·06	0·33	0·05	0·28	0·048	0·27
ClNa	0·06	0·33	0·055	0·31	0·058	0·32
$ClNH_4$	0·045	0·25	0·040	0·22	0·035	0·19
	30°C.		40°C.		50°C.	
	in cc.	%	in cc.	%	in cc.	%
$C_{12}H_{22}O_{11}$	0·17	0·94	0·17	0·94	0·17	0·94
ClK	0·048	0·27	0·044	0·24	0·045	0·25
ClNa	0·05	0·28	0·035	0·19	0·04	0·21
$ClNH_4$	0·030	0·17	0·035	0·19	0·030	0·16

In spite of the fact that the above values are merely approximate, it is clear that the amount of volume change of solvent depends on the nature of the solutes. In the above data, the compression of the solvent is greatest in the case of cane sugar as solute; it is less and nearly equal in the case of potassium chloride and sodium chloride,

and least in the case of ammonium chloride. In all the cases the degree of compression becomes smaller and smaller as the temperature rises. From this record of the compressibility of solvents, any quantitative relation can not be found with certainty, but it may be supposed that the compressibility is a function of the molecular weight, M, and the molecular volume, V, something like $\frac{\varphi(M)}{f(V^{\frac{2}{3}})}$.

The volume change of the solute in solution. In solution, as the solute and solvent are only relative terms, what has been said about solvent may equally well be applied to the case of solute. As seen in Figg. 4–6, the molecular solution volume of solute increases with the increase of concentration while its rate of increase derceases with the increase of the concentration.

The dilatation of the solute with concentration is as follows:

TABLE 34.

	a in cc.	*b* in cc.	Difference.	Percentage.
		0·0°C.		
$C_{12}H_{22}O_{11}$	212·5	216·1	3·6	1·68
ClK	29·	30·8	1·8	6·02
ClNa	18·2	20·0	1·8	9·43
$ClNH_4$	37·5	38·5	1·0	2·6
		10·0°C.		
$C_{12}H_{22}O_{12}$	214·0	217·1	3·1	1·44
ClK	30·0	31·6	1·6	5·2
ClNa	19·2	20·7	1·5	7·9
$ClNH_4$	38·2	39·0	0·8	2·1
		20·0°C.		
$C_{12}H_{22}O_{11}$	215·3	218·0	2·7	1·25
ClK	30·6	32·0	1·4	4·4
ClNa	19·2	20·7	1·5	7·5
$ClNH_4$	38·6	49·3	0·7	1·8
		30·0°C.		
$C_{12}H_{22}O_{11}$	216·4	219·0	2·6	1·2
ClK	31·0	32·2	1·2	3·8
ClNa	20·6	21·8	1·2	5·6
$ClNH_4$	38·8	40·1	1·3	3·4

		40·0°C.		
$C_{12}H_{22}O_{11}$	217·3	219·9	2·6	1·2
ClK	31·4	32·4	0·0	3·1
ClN_2	20·9	22·0	1·1	5·2
$ClNH_4$	39·0	40·3	1·3	3·3
		50·0°C.		
$C_{12}H_{22}O_{11}$	218·3	220·8	2·5	1·1
ClK	31·6	32·6	1·0	3·1
ClNa	21·2	22·5	1·0	4·6
$ClNH_4$	39·0	40·4	1·4	3·5
		60·0°C.		
$C_{12}H_{22}O_{11}$	219·3	221·7	2·4	1·1

In the above table a and b are the molecular solution volumes of the solute at 1·5 and 2·5 molar concentration respectively, and percentages of dilatation are the percentage values of $a-b$ in $\frac{a+b}{2}$. The compressibility of the solvent expressed in the terms of pressure is tolerably great, but not so great that we can not admit it as an inner pressure[1] of solution; but, if solutes are in the same state of aggregation in solutions as in the pure state, the dilatation of the solutes, in the terms of pressure becomes so great that it can not be admitted as inner pressure of solution. According to the research of T. R. Richards,[2] the compressibility of the following salts in 100–500 megbars are as follows:

Compressibilities × 10^6 at 20·0°C°.

	Kgm/cm².	Megbars.	Atmosphere.
ClK	4·93	5·03	5·09
ClNa	4·03	4·11	4·17

Therefore, to produce such volume change as is represented in the table 34, the inner pressure must be of the order of 10^4 atm., but it is not reasonable to assume the existence of such a great pressure in solution. To explain this contradiction, it may be supposed that the molecular state of aggregation of a solute in solution is different

1 *See* the following paragraph.

2 J. Amer. Chem. Soc., **31**, 158 (1909).

from that in its pure state. It is generally accepted that the phenomena "dissolution" is nothing but the disintegration of the solute in the solvent to its molecular order by the mutual affinity of the solute and solvent. Then solute molecules, occluded by solvent molecules, are compressed and diminish their volumes. But this kind of compression is not the only cause of the change of volume of solute in solution; the volume changes due to ionisation or polymerisation would perhaps play a great rôle for volume change of solute in solution. This supposition explains why the dilatation of cane sugar, which is a non-electrolyte, is less than that of electrolytes.

The change of molecular solution volume in lithium chloride solution is represented in Fig. 7. It is well known that lithium chloride polymerizes in solution; and, since ionisation and polymerization take place in its solution at the same time the matter becomes somewhat more complicated in this case. As seen in the figure the volume changes of both of solute and solvent are great in dilute solutions and become less with the increase of concentration.

From the above point of view about the change of molecular soiution volumes in solution, arise certain interesting problems, such as the inner pressure of solution by the mutual compression of solute and solvent and the molecular solution volume of its solute in a saturated solution. These will be considered in the following paragraphs.

6. Inner Forces of Solution and Molecular Pressure.

Tammann,[1] who assumed some inner force acting in solution studied the problem of solution from a standpoint entirely different from that of van't Hoff and Arrhenius. The change of specific volume of solution by temperature proceeds in quite the same way as that of the pure solvent by some external pressure, and then the concentration of solution is comparable to external pressure on solvent as to its influence on volume. Now, the change of specific volume of solution with the change of temperature in several concentration is first determined and then the external pressure is calculated under which the pure solvent undergoes the same change of volume as the solution; these pressures as the inner pressure forces of solution are denoted by $\triangle K$ in the terms of pressure. By dividing these terms by the concentrations of the corresponding solutions m, we get values which are con-

1

stant and independent of concentration for solutions of the same solute. Tammann used this expression, $\triangle K/m$, for comparison of several solutions of different solutes.

The idea of some inner force acting in solution is of value in the study of solution; but the inner force defined by Tammann can not be considered a real existing force, because, while the volume of solute is tolerably great with respect to the total volume in concentrated solutions, Tammann's inner force is also estimated by a direct comparison of the total volume of solution to that of the pure solvent; and this is the same as to neglect the volume of solute in solution.

In the present study, the volume of solute in solution has already been estimated, therefore it is possible to calculate the amount of external work required to effect such a volume change on the pure solute as that in solution: and it is more reasonable than Tammann's method to consider this pressure as the inner pressure acting in solution.

In the following table, the molecular volume of water at 0°C. being taken as unity, those in solution in different concentrations at different temperatures were calculated and denoted by v; and then the external pressure P, required to effect such volume change as v, were calculated from the data of dilatation and compressibility of water given by Amagat.[1] Theoretically the value P diminished by one atmosphere must be taken as the inner pressure of the solution, but such correction is not necessary as it is within the uncertainty of calculated results.

TABLE 35.

The solution of Cane Sugar at 0·0°C.

Mean conc.	φ_w	v	P. atm.
0·075	18·019	1·0000	1
0·227	18·015	0·99977	4·5
0·469	18·004	0·99917	16·0
0·814	17·986	0·99816	36·0
1·188	17·968	0·99717	55·0
1·596	17·891	0·99289	141·5
2·040	17·804	0·98808	241·2
2·395	17·719	0·98334	342·5
2·524	17·700	0·98229	365·
2·648	17·665	0·98037	407·5

1 C. R., **116**, 41 (1893).

TABLE 36.

The Solution of Cane Sugar at 10·0°C.

Mean conc.	φ_m	v	*P.* atm.
0·075	18·021	1·00014	1
0·226	18·019	1·00000	3
0·469	18·018	0·99995	4·5
0·812	17·998	0·99883	27
1·165	17·970	0·99728	59·5
1·591	17·920	0·99450	119
2·0335	17·844	0·99039	208
2·387	17·767	0·98624	301
2·515	17·737	0·98435	345
2·638	17·701	0·98235	391

TABLE 37.

The Solution of Cane Sugar at 20·0°C.

Mean conc.	φ_m	v	*P.* atm.
0·074	18·048	1·00164	1
0·226	18·047	1·0016	1·5
0·467	18·042	1·0013	7
0·810	18·029	1·0006	21
1·162	18·004	0·99920	51·5
1·582	17·959	0·99671	106·5
2·026	17·890	0·99286	193·5
2·378	17·818	0·98887	286
2·506	17·790	0·98732	323
2·628	17·760	0·98562	263

TABLE 38.

The Solution of Cane Sugar at 30·0°C.

Mean conc.	φ_m	v	*P.* atm.
0·074	18·094	1·00421	1
0·225	18·092	1·0041	3
0·466	18·087	1·0038	9·5
0·807	18·074	1·0031	24
1·177	18·045	1·0015	58

Mean conc.	φ_m	v	P. atm.
1·580	18·018	0·99996	93
2·018	17·955	0·99651	172·5
2·369	17·883	0·99248	267
2·496	17·855	0·99092	304·6
2·618	17·823	0·98919	346·5

TABLE 39.

The Solution of Cane Sugar at 40·0°C.

Mean conc.	φ_m	v	P. atm.
0·074	18·157	1·00757	1
2·250	18·151	1·0073	6
0·465	18·145	1·0069	15
0·804	18·132	1·0062	28
1·173	18·113	1·0047	63·5
1·574	18·092	1·0040	79
2·010	18·019	0·99993	173
2·359	17·953	0·99628	260
2·486	17·927	0·99485	295
2·607	17·895	0·99307	339

TABLE 40.

The Solution of Cane Sugar at 50·0°C.

Mean conc.	φ_m	v	P. atm.
0·074	18·233	1·01182	1
0·386	18·229	1·0116	6
0·463	18·224	1·0113	12
0·801	18·215	1·0108	23
1·168	18·196	1·0097	46
1·567	18·160	1·0078	78
2·001	18·096	1·0042	172
2·349	18·031	1·0006	257
2·475	18·008	0·99931	289
2·596	17·980	0·99774	328

TABLE 41.

The Solution of Cane Sugar at 60·0°C.

Mean conc.	φ_m	v	P. atm.
0·073	18·322	1·01678	1
0·223	18·320	1·0167	3
0·460	18·317	1·01655	6
0·797	18·314	1·0164	9
1·162	18·293	1·0152	35
1·559	18·250	1·0128	87
1·992	18·190	1·0095	161
2·338	18·125	1·0052	263
2·464	18·104	1·0047	275
2·584	18·078	1·0033	309

TABLE 42.

The Solution of Potassium Chloride at 0·0°C.

Mean conc.	φ_w	v	P. atm.
0·347	18·019	1·0000	1
1·063	17·989	0·99837	32
1·826	17·941	0·99559	87
2·638	17·894	0·99307	138

TABLE 43.

The Solution of Potassium Chloride at 50·0°C.

Mean conc.	φ_m	v	P. atm.
0·342	18·233	1·01182	1
1·047	18·226	1·0114	9
1·795	18·185	1·0091	60
2·591	18·163	1·0079	87
3·437	18·11	1·0050	154
4·067	18·07	1·0027	207

TABLE 44.

The Solution of Sodium Chloride at 0·0°C.

Mean conc.	φ_m	v	P. atm.
0·444	18·019	1·00000	1
1·365	17·979	0·99779	45
2·352	17·915	0·99426	113·5
3·400	17·840	0·99008	198
4·301	17·755	0·98533	295
5·006	17·723	0·98360	337

TABLE 45.

The Solution of Souium Chloride at 50·0°C.

Mean conc,	φ_m	v	P. atm.
0·437	18·233	1·01182	1
1·342	18·212	1·0103	33
2·308	18·178	1·0078	90
3·330	18·137	1·0065	119
4·209	18·07	1·0027	207

TABLE 46.

The Solution of Ammonium Chloride at 0·0°C.

Mean conc	φ_m	v	P. atm.
0·467	18·019	1·00000	1
1·429	18·012	0·99960	8·5
2·434	17·96	0·9970	59
3·454	17·91	0·9940	119

TABLE 47.

The Solution of Ammonium Chloride at 50·0°C.

Mean conc.	φ_w	v	P. atm.
0·469	18·232	1·01182	1
1·420	18·213	1·0107	24
2·397	18·177	1·0087	69
3·399	18·14	1·0053	149·5
4·427	18·09	1·0037	185
5·478	18·07	1·0027	207

The inner pressures as calculated above as a function of concentration were represented graphically in Figg. 8–9. When the solution is dilute, the increase of inner pressure by the increase of concentration is slow, but at the vicinity of 1·5 molar concentration the pressure suddenly increases and thereafter nearly as a linear function of concentration. The increase of inner pressure corresponding to the increase in concentration by one molal in the range of the inner pressure which is directly proportional to the concentration may be termed "*molecular pressure in solution*". This is a factor of physico-chemical affinity of solution.

TABLE 48.

Solution.	Temperature.	Mol. pressure in atm.
$C_{12}H_{22}O_{11}$	0°–60°	220·
ClK	0°–50°	130·
ClNa	0°–50°	130·
$ClNH_4$	0°–50°	150·

A comparison of the kinds of pressures, that is, osmotic pressure, Tammann's inner force and the author's inner pressure.

TABLE 49.

Tammann's Inner Forces of Solutions.

A) *Cane Sugar Solution.*

Temperature 10°–30°.

m	4·75	9·50	19·00	38·00	76·00
$\triangle K$	105·	218·	408·	700·	1217·
$\frac{\triangle K}{m}$	22·	23·	22·	23·	16·

B) *Potassium Chloride Solution.*

Temperature 10°–30°.

m	5·2	11·2	16·8	17·9	22·5	23·2	33·4	33·7
$\triangle K$	312·	607·	850·	916·	1080·	1126·	1345·	1380·
$\frac{\triangle K}{m}$	60·	55·	55·	51·	48·	49·	40·	41·

C) *Sodium Chloride Solution.*

Temperature 10°–30°.

m	1·61	3·24	6·48	12·96	25·93
$\triangle K$	182·	336·	665·	1217·	2145·
$\frac{\triangle K}{m}$	113·	104·	103·	94·	83·

D) *Ammonium Chloride Solution.*

Temperature 10°–40°.

m	11·1	25·0
$\triangle K$	628·	1018·
$\frac{\triangle K}{m}$	57·	36·

Tabulation of the osmotic pressure of aqueous solutions of cane sugar determined by Morse and Lord Berkeley and Hartley.

TABLE 50.[1]

No. of mols	Osmotic pressure at 0°C.	
in litre.	(Morse.)	(Lord Berkeley and Hartley.)
0·527	—	13·95
0·534	14·38	—
0·646	19·48	—
0·828	24·83	—
0·877	—	26·77
1·228	—	43·97
1·579	—	67·51
1·930	—	100·78
2·194	—	133·74

These values of the three kinds of pressures are represented in Figg. 8–9. The inner pressure determined by the author is less than Tammann's inner force but is greater than osmotic pressure directly determined. In dilute solutions the inner pressure is nearly equal to the osmotic pressure. The relation between this inner pressure and osmotic pressure will be considered in the next article of this study.

1 Findlay: Osmoitc Pressure, p. 23.

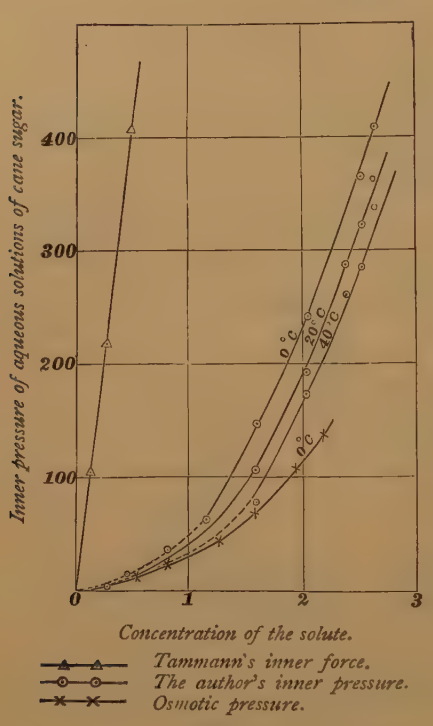


Fig. 8.

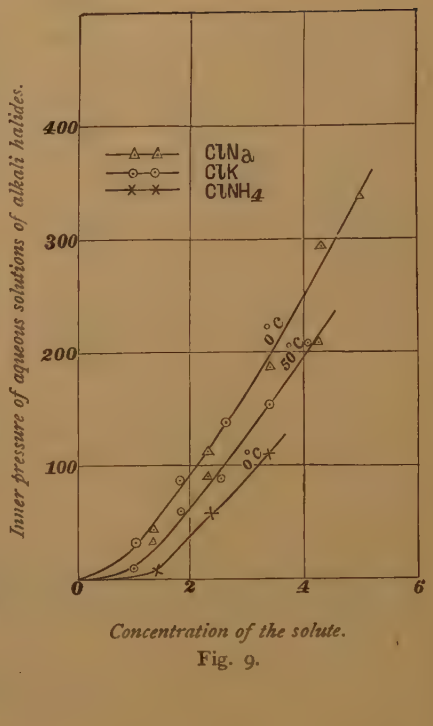


Fig. 9.

7. The Relation between the Solubility and the Molecular volumes of Solutes.

The solubility of a solute in a given solvent is one of the physico-chemical properties which is characteristic of that solute. But solubility depends on many factors and is of very complex nature; therefore at present there is no simple relation established between it and the other properties of said solute or solvent; in other words, there is no quantitative theory of solubility.

Hardman and Partington[1] have found a relation of solubility to temperature applying Kirchhoff's law, as follows:

$$\log S = A - \frac{B}{T} - C \log T,$$

where S is the solubility and A, B, and C are constants characteristic of the solute. But, since this equation contains three constants, there is no difference in value from the empirical formula: $S = A + BT + CT^2$

[1] J. Chem. Soc., **99**, 1769 (1911).

as Tyrer[1] remarked. From the study of solubilities at critical temperatures, Tyrer has fonnd the following relation:

$$S^n = a\left(\frac{V}{v}\right)^n - b,$$

where n is a certain constant, V the total volume of solution, v the specific volume of solute and a and b are constants characteristic of a given solute and solvent. But there are no sufficient data to verify this equation.

Under the supposition that there would be some definite relations between the molecular volumes of substances and their solubilities in water, the author examined the solubilities of sparingly soluble organic liquids in water. For such substances, it may be assumed that their molecular volumes in saturated solution are not greatly different from those in the pure state and therefore that they may be put equal to each other. But in literature, the determination of the solubilities of such substances are infrequent, and only the data on alkyl halides by A. Rex[2] are appropriate. The solubilities and molecular volumes of alkyl halides are tabulated as follows:

TABLE 51.

0.0°C.

	Substance.	Mol. wt. M	Solubility. S	Sp. gr.	Mol. vol. V
1.	Methylene chloride	84·9	2·363	1·37777[B]	61·6
2.	Chloroform	119·4	1·062	1·52637[B]	73·3
3.	Tetrachlormethane	153·8	0·097	1·63195[B]	94·4
4.	Methylene bromide	173·9	1·173	—	—
5.	Methyl iodide	141·9	1·565	2·3346[B]	60·8
6.	Ethylene chloride	98·9	0·922	1·28032[B]	77·2
7.	Ethylidene chloride	98·9	0·656	1·2044[B]	82·0
8.	Ethyl bromide	109·0	1·067	1·496439[B]	73·0
9.	Ethyl iodide	155·9	0·441	1·9845[C]	78·4*
10.	Propyl chloride	78·5	0·376	0·9156[B]	85·8
11.	Isopropyl chloride	78·5	0·440	—	—
12.	Propyl bromide	123·0	0·298	1·383[B]	88·6

1 J. Chem. Soc., **97**, 621, 1778 (1910); J. phys. Chem., **16**, 69 (1912).

2 Z. physik. Chem., **55**, 355 (1906).

B *From* Beilstein's Organische Chemie.

C *From* Tables annuelles internationalles de Constantes, Vols. I–III.

	Substance.	Mol. wt. M	Solubility. S	Sp. gr.	Mol. vol. V
13.	Isopropyl bromide	123·0	0·418	$1\ 3583^{B}$	90·5
14.	Propyl iodide	170·0	0·114	$1·784^{B}$	95·4
15.	Isopropyl iodide	170·0	0·167	—	—
16.	Carbon disuphide	76·1	0·248	$1·2905^{B}$	58·9*

TABLE 52.

20·0°C.

	Substance.	Mol. wt.	Solubility. S.	Sp. gr.	Mol. vol. V.
1.	Methylene chloride	84·9	2·000	—	—
2.	Chloroform	119·4	0·822	$1·4868^{1}$	80·4
3.	Tetrachlormethane	153·8	0·080	$1·5930^{1}$	96·5
4.	Methylene bromide	173·9	1·148	$2·488^{B}_{Extrap.}$	69·8
5.	Methyl iodide	141·9	1·419	$2·269^{B}_{Extrap.}$	62·5
6.	Eihylene chloride	98·9	0·869	$1·254^{B}_{Mean}$	78·8
7.	Ethylidene chloride	98·9	0·550	$1·1743^{B}$	84·2
8.	Ethyl bromide	109·0	0·914	$1·4580^{1}$	74·7
9.	Ethyl iouide	155·9	0·403	$1·9387^{1}$	80·4*
10.	Propyl chloride	78·5	0·272	ca. $0·892^{B}$	82·6
11.	Isopropyl chloride	78·5	0·305	$0·8588^{B}$	91·4
12.	Propyl bromide	123·0	0·245	$1·3520^{B}$	90·8
13.	Isopronyl bromide	123·9	0·318	$1·3097^{B}$	93·8
14.	Propyl iodide	170·0	0·107	$1·7427^{B}$	98·6
15.	Isopropyl iodide	170·0	0·140	$1·7033^{B}$	99·8

TABLE 53.

30·0°C.

	Substance.	Mol. wt. M	Sclubility. S	Sp. gr.	Mol. vol. V
2.	Chloroform	119·4	0·776	$1·4680^{1}$	81·4
3.	Tetrachlormethane	153·8	0·085	$1·5757^{1}$	97·7
4.	Methylene bromide	173·9	1·176	ca. $2·466^{B}_{Extrap.}$	70·5
5.	Methyl iodide	141·9	1·429	ca. $2·237^{B}_{Extrap.}$	63·5
9.	Ethyl iodide	155·9	0·415	$1·911^{1}_{Extrap.}$	81·5

B *From* Beilstein's Organische Chemie.

1 *From* Tablas annuelles internationales de Constantes, Vols. I–III.

Fig. 10.

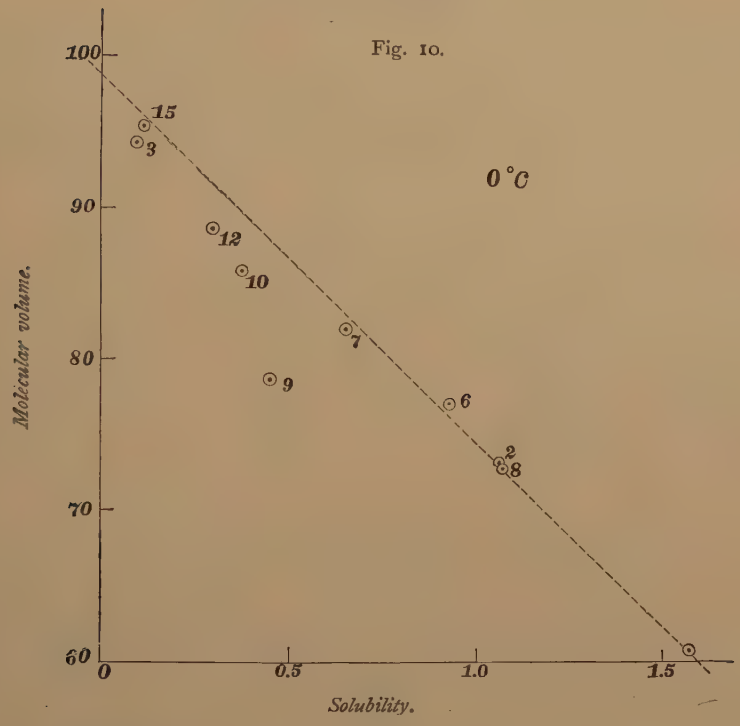
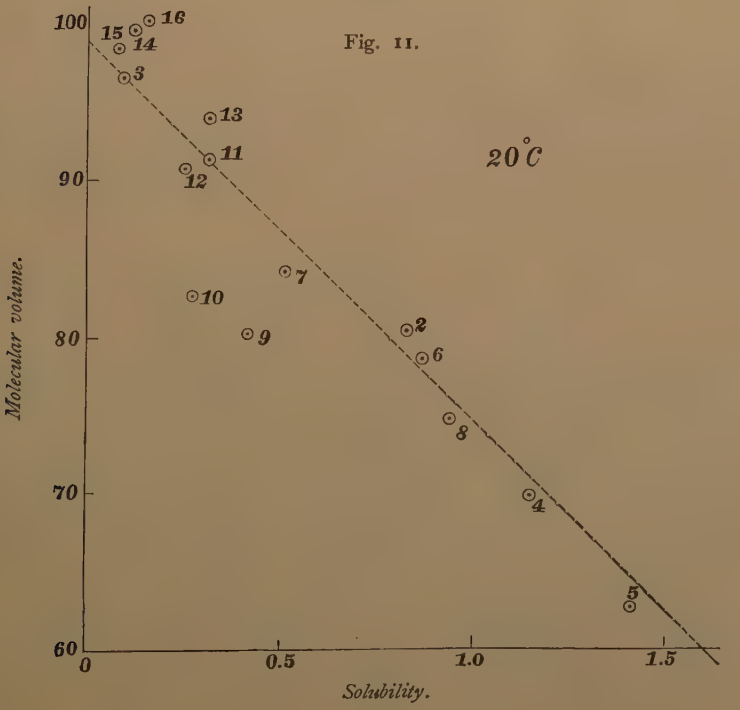

100
90
80
70
60
0
0.5
1.0
1.5
Molecular volume.
Solubility.
0 °C
15
3
12
10
7
9
6
2
8

Fig. 11.


100
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1.5
Molecular volume.
Solubility.
20° C
16
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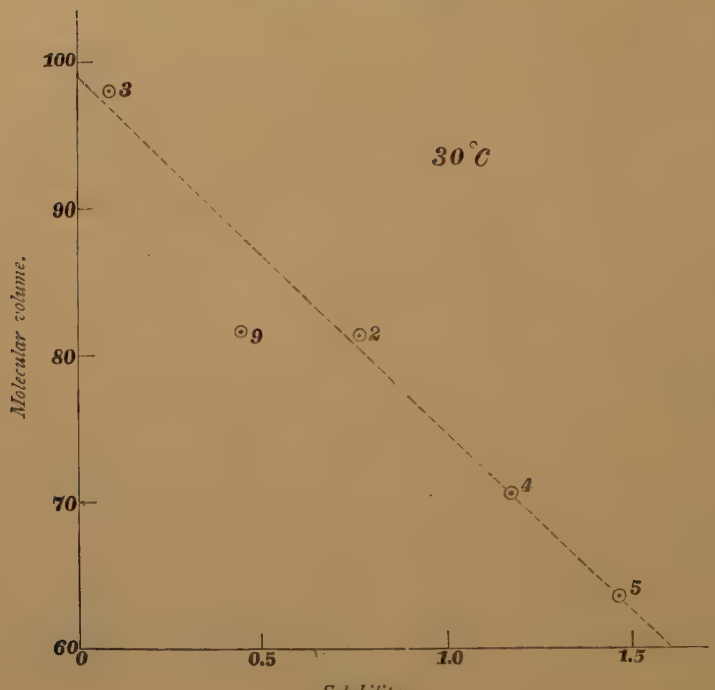


Fig. 12.

Representing the above relations graphically in Figg. 10–12 as usual, it appears that solubility and molecular volume are in a simple linear relation and moreover that this relation holds at different temperatures, as 0°, 20°, and 30°C. This may be expressed by the following equation:

$$S = -\frac{1{\cdot}60}{99{\cdot}0} + 160,$$

or

$$\frac{S}{M} = N = -\frac{1{\cdot}70}{99{\cdot}0} \cdot \frac{V}{M} + \frac{1{\cdot}60}{M},$$

where S denotes the solubility and M the molecular weight of solute; and in dilute solutions, N will be proportional to the number of mols in solution. Methylene chloride and ethyl iodide show great deviation from this formula; and carbon disulfide also shows a great deviation, and perhaps for the reason that the latter is of a different class from alkyl halides and wherefore has a different affinity to water.

The relation of solubility here set forth may be the first quantitative one ever proposed, and is too regular to appear accidental. It seems very desirable to continue the research concerning this relation

in other homologous series; and such is the writer's intention; but for the present it is impossible to procure the necessary materials. Certain experiments have been made on hydrocarbons of benzene series; and the solubilities and molecular volumes obtained are given in the following table.

TABLE 54.

Temperature: 20·0°C.

Substance.	Mol. weight.	Solubility.	Sp. volume.	Mol. volume.
Benzene	78·1	0·181	0·87873	88·9
Toluene	92·1	0·063	0·86675	106·3
Xylene	106·1	0·018	0·86081	123·2
Mesitylene	120·1	ca. 0·002	0·8558	140·2

In the case of hydrocarbons of benzene series also, the solubility decreases with the increase of molecular volume; but it does not show such an interesting result as in the case with alkyl halides, because, in the latter case quite independent of the magnitude of the molecular weight, the solubilities are always in the reverse order of molecular volumes, while in the former case, the molecular weight and molecular volume are, from the first, in the same order.

Considering what relation may exist with a substance that has great solubility, the molecular solution volume in saturated solution of cane sugar and alkali chlorides may easily be estimated by graphical extrapolatiou from the data already found.

TABLE 55.

A) *Aqueous Solution of Cane Sugar.*

Temperature.	Solubility. No. of grs. of solute in 100 grs. of solution.	Sp. gravity of saturated solution.	Mol. concentration of saturated solntion.	Mol. sol. vol. estim. by extrapolation.
0°	64·18	1·321	2·477	216·
10°	65·58	1·325	2·539	217·
20°	67·09	1·329	2·605	218·3
30°	68·70	1·334	2·679	219·5
40°	70·42	1·339	2·755	220·5
50°	72·25	1·344	2·837	221·5
60°	77·18	1·350	2·926	222·5

B) *Aqueous Solution of Potassium Chloride.*

Temperature.	No. of grs. of solute in 100 grm. of solubility, solution.	Sp. gravity of saturated solution.	Mol. concentration of saturated solution.	Mol. sol. vol. estim. by extrapolation.
0°	21·6	1·151	3·33	32·
10°	23·7	1·1635	3·70	32·8
20°	25·4	1·171	3·99	33·5
30°	27·1	1·180	4·28	33·5
40°	28·6	1·186	4·55	34·
50°	29·9	1·190	4·77	34·

C) *Aqueous Solution of Sodium Chloride.*

0°	26·28	1·209	5·434	23·
10°	26·29	1·204	5·416	23·
20°	26·37	1·200	5·414	23·5
30°	26·49	1·195	5·417	23·5
40°	26·65	1·191	5·430	24·
50°	26·83	1·186	5·445	24·

D) *Aqueous Solution of Ammonium Chloride.*

0°	22·7	1·072	4·54	40·
10°	24·9	1·074	5·00	40·
20°	27·1	1·076	5·44	41·
30°	29·3	1·078	5·91	41·
40°	31·4	1·080	6·34	41·
50°	33·5	1·081	6·77	41·

E) *Aqueous Solution of Lithium Chloride.*

0°	40·1	1·261	11·90	ca. 21·4
10°	41·9	1·271	12·56	21·4
30°	45·8	1·298	14·03	21·4
50°	49·2	1·33	15·44	21·4

As seen from the above table, the molecular solution volume of the solute in saturated solutions, at different temperatures do not differ much from each other, and are almost independent of temperature.

A comparison of the molecular volumes of solute in solid states and the molecular solution volumes in saturated solutions. At present, the

molecular condition of substance in a solid state is not so exactly defined as in a gaseous state or in solution; and here the molecular volume of a solid substance is calculated under the assumption of the existence of normal molecules, as suggested from the chemical formula.

	Mol. wt.	Sp. gr.	Mol. vol.
ClK	74·55	2·00	37·3
ClNa	58·46	2·14	27·3
$ClNH_4$	53·50	1·51	35·4
ClLi	42·40	2·07	20·5

In the case of cane sugar, as its coefficient of expansion is comparatively great, its specific gravities at different temperatures were determined in a specific gravity bottle using xylene (boil. pt. 159°C.) as the filling liquid.

Temperature.	Sp. gr. of xylene.	Sp. gr. of cane sugar.
20°	0·86122	1·5869
30°	0·85260	1·5885
40°	0·84418	1·5833
50°	0·83521	1·5810

By the help of Morse's value of the specific gravity 1·59231 at 0°C., the specific gravity at 10°C. has been estimated by graphical interporation, to be 1·590, and from these data the molecular volumes of cane sugar in solid state has been calculated as follows:

Temperature.	Mol. vol.	Temperature.	Mol vol.
0°	214·4	30°	215·8
10°	215·2	40°	216·2
20°	215·6	50°	216·4

Now on comparing the molecular volumes of solutes in solid state with molecular solution volumes in solutions, it may be clearly seen that in all cases, the molecular solution volumes in saturated solutions are very far nearer to molecular volumes in solid state than molecular solution volumes in dilute solutions. The molecular solution volumes in saturated solutions are less than the molecular volumes in solid state in the cases of potassium chloride and sodium chloride, and are little larger in ammonium chloride and cane sugar, and are equal to in lithium chloride.

From the above few experimental results, it is not desirable to build up any hypothesis, but perhaps it may be said that, in solutions, the molecular solution volume of the solute approaches to molecular volume in solid state by the increase of concentration.

If the molecular solution volumes in solution determine the state of saturation, then the saturation or solubility is also determined by physico-chemical affinity between solute and solvent, as the change of molecular solution volume is caused by that physico-chemical affinity.

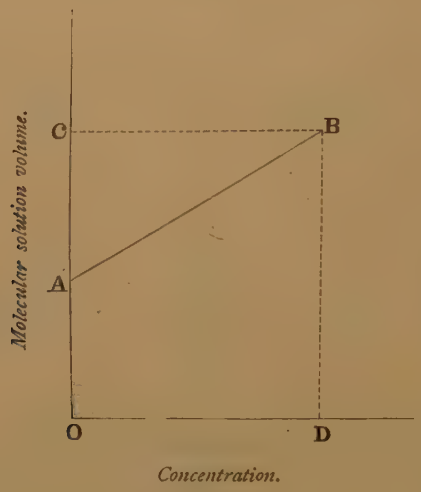


Fig. 13.

To illustrate the relation between them, Fig. 13 was constructed, measuring the molecular solution volume of the solute along the axis of ordinates and the concentration along the axis of abscissa. Thus *AB* represents the change of the molecular solution volume of the solute as the concentration increases, *DB* and *OD* being respectively the molecular volume in and concentration of the saturated solution. Now, if the molecular volume of solute in a saturated solution has a definite value *DB*, the concentration of the saturated solution would be determined only by the two factors, the inclination of *AB* and the length of *CA*, *CB* being a parallel to *OD*, and these two also depend on the physico-chemical affinity between the solute and solvent. Then the solubility of any substance would depend on its physico-chemical affinity to the solvent and it is difficult to represent its solubility as a single function of another physical constant of the solute or solvent. But in the case of halogen alkyls, whose affinities to the solvent would

not much differ among themselves, a simple relation between solubility and molecular volume as above described will be expected.

8. A Conception on the State of Solution.

From what has been said above, the following conclusion has been drawn as to the state of solution.

When a substance is dissolved in a solvent, change in molecular solution volumes of the solute and solvent generally takes place by the physico-chemical affinity between the solute and solvent; the molecular solution volume of the solute increases with the increase of its concentration, while the molecular solution volume of the solvent decreases as the concentration increases. When the molecular solution volume of the solute reaches a certain definite value, the solution becomes saturated and this molecular solution volume in the saturated solution is almost equal to the molecular volume of the solute in a pure state.

9. Summary.

1. The method of determination of the molecular solution volumes of solute and solvent in solution has been described.

2. By this method of determination, the molecular solution volumes of cane sugar, potassium chloride, sodium chloride, ammonium chloride, and lithium chloride in aqueous solutions in several temperatures have been determined.

3. The compression of molecular solution volume of solvent by the action of solute molecules has been represented in pressure terms and it was compared with osmotic pressure directly determined and Tammann's inner force of solution.

4. Some relations between the molecular volume of a solute and its solubility have been pointed out.

5. As the conclusion of the above experimental results, a conception on the state of solution has been proposed.

I desire to express my cordial thanks to Prof. Osaka for the interest he has taken in my work and for his valuable advice.

Studies of Solution. II.

A Conception of Osmotic Pressure.

By

Shinkichi Horiba.

(Received Oct. 12, 1916).

In the present article, the theory of osmotic pressure will be considered and a new conception of that pressure be presented according to the hypothetical figure of solution attained from the studies of molecular solution volumes of solute and solvent in solution and reported in the preceding article.

The theory of osmotic pressure of solution given by van't Hoff has played a prominent part in the development of physical chemistry, and several conceptions have been proposed concerning the nature of that pressure, but as yet none are satisfactory.

This problem may conveniently be treated separately in two parts, that is :

1. The action of a semipermeable membrane ;
2. The mechanism of the existence of the pressure difference between a solution and the pure solvent.

The osmotic phenomena, however, can not naturally be separated in such a way, and especially for the study of the first part, the experimental results of the second part must be taken into consideration. The study of the second part may be carried on without regard to the first part and independent of the nature of the action of the semipermeabie membrane, and indeed, van't Hoff's theory concerns only the second part of the problem. Here also only the second part is taken into consideration with an assumption of the possibility of a perfect semipermeable membrane and without inquiry as to what theory, atomic sieve, solution, absorption,[1] or capillary, may be true as to the nature of the action of a semipermeable membrane.

1 Recently F. Tinker (Proc. R. Soc. London **4**, 92. (1916)) studied the structures of semipermeable membranes and supported adsorption theory of osmosis.

In the famous work of van't Hoff[1] „Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen" the following words are found in its beginning:

„Bei einer Untersuchungen, die im wesentlichen Kenntniss der chemischen Gleichgewichtsgesetze in Lösungen bezweckte, hat sich allmählich herausgestellt, dass eine tiefgehende Analogie, ja fast Identität mit den Gasen, speziell auch in physikalischer Beziehung, vorliegt, falls nur bei Lösungen vom sogenanten osmotischen Druck die Rede ist, da wo es sich bei Gasen um den gewöhnlichen Spannkraftdruck handelt." The important conclusion of this paper is: Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert they were gassified at the same temperature without change of volumes; and this is expressed in the simple equation

$$PV = nRT$$

where P denotes osmotic pressure, V total volume of solution, n number of mols of solute, and R the gas constant.

From this paper of van't Hoff, we see, that the simple mathematical relation given above is an experimental fact which, therefore, admits no discussion. But as to the analogy between solution and gaseous state there may be some discussions because, though the state of solution and that of gas were quite different, it is not to be denied that in some cases an accidental coincidence of the mathematical equations of the two states may occur.

Fig. 1.

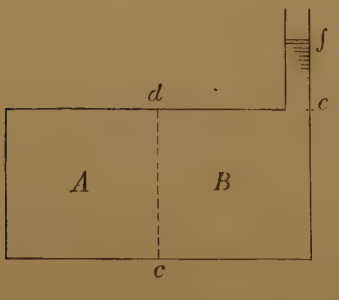
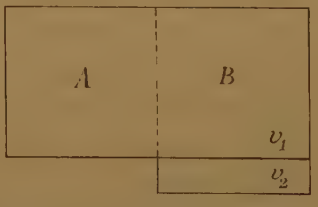


Fig. 2.



In Fig. 1, if A be a pure solvent, say water, B a solution, say aqueous solution of cane sugar, and cd a perfect semipermeable membrane, then a certain quantity of solvent will penetrate into solution

[1] Zs. physik. Chem. I, 481 (1887).

through the membrane *cd*, and a hydrostatic pressure will be produced in the solution as shown by *ef* in the figure. The pressure which is acting on the semipermeable membrane, that is the so called osmotic pressure, is usually determined from this hydrostatic pressure. If the analogy between the gaseous state and the solution were established, the above osmotic pressure should be considered as the effect of the kinetic motion of the solute molecules.

Now, for a comparison, let us consider a gaseous mixture. In Fig. 2. A and B were first equally filled, with pure oxygen under one atmosphere pressure; and then a certain quantity of nitrogen under one atmosphere was added to B. After mixing, to maintain the total pressure of B still at one atmosphere, the volume of B must be enlarged by the volume of nitrogen added. If *cd* be a hypothetical semipermeable membrane through which oxygen will pass but nitrogen not, since the partial pressure of oxygen in B is lower than in A, a certain amount of oxygen in A will penetrate into B through the membrane *cd* until the partial pressure of oxygen becomes equal on the both sides of the membrane. Let v_1 and v_2 be the volumes of oxygen and nitrogen in B respectively. If an external pressure be added and v_1+v_2 be compressed to v_1, the oxygen in A will be in equiliblium with that of B without any passage of oxygen throngh the membrane. If the external pressure at first be $P_1=1$, then from the gas law, the following relation is obtained:

$$(v_1+v_2)\,P_1 = v_1(P_1+P_2),$$

therefore

$$v_2P_1 = v_1P_2 = nRT,$$

$$P_2 = \frac{n}{v_1}RT.$$

P_2 is what is analogous to osmotic pressure in solution. In the case of solution, the external pressure is generally $P_1=1$. Thus to establish the equilibrium between the solution and solvent through a semipermeable membrane, an additional external pressure P_2, must be applied on the side of solution; otherwise, a certain quantity of the solvent would penetrate into the solution, and the equilibrium state is attained and a certain hydrostatic pressure is reached in the solution. From such considerations it seems that there is no contradiction to the analogy between the gaseous state and solution.

Further, let us see how much compression is necessary to establish equilibrium between the solution and the pure solvent through a

semipermeable membrane. The following data from Morse's[1] experiments on cane sugar solution, may be considered.

Aqueous Solution of Cane Sugar at 0°C.

Weight normal conc.	Volume of solvent.	Volume of solute.	Sum.	Volume of solution.	Difference.	Contraction. %	Osmotic pressure obs
0·1	1000·13	21·328	1021·458	1020·73	0·728	0·07	(2·462)
0·5	,,	106·640	1106·770	1103·01	3·760	0·37	11·895
1·0	,,	213·280	1213·410	1206·69	6·720	0·55	24·826

As shown in the table, the contraction accompanying the formation of solution of one weight normal concentration, is only 0·55% ; and, if we take into consideration the analogy between the gaseous state and solution, it must be concluded that this solution receives an osmotic pressure of 24·826 atm. by the additional compression from 1206·69 cc. to 1000·13 cc. or of 20·7%. There is no known data concerning the compressibility of cane sugar solution ; but it may be supposed to be less than that of water. As to the compressibility of water, there is the well known investigation by Amagat[2] ; according to which, for a compression of 2·8% of a volume of water at 0°C., a pressure of 600 atm. was needed. Thus it is impossible to consider that the directly measured osmotic pressure of about 25 atms. could counterbalance the above stated compression of cane sugar solution. This may be explained as follows. In a gaseous state the actual volume of gas molecules is very small in comparison to this apparent volume, while in solid state, such as cane sugar, on the contrary the actual volume of the molecules is equal or very nearly equal to the apparent volume. Taking this difference between gaseous and solid states into consideration, it may be assumed that the dissolution of cane sugar in the solvent would not much increase the free volume for the motion of the solvent molecules, and in that case the osmotic pressure equilibrium would be established by a little compression.

This explanation may perhaps be correct ; but, if the consideration that the free volume is very small or does not exist in solid state is admissible, there is no reason to doubt that the same conception might be applied to the state of liquid. The term "b" in van der Waals' equation gives us an idea of actual volume of gaseous and

1 The Osmotic Pressure of Aqueous Solution, p. 104.

2 C. R., **116**, 41 (1893).

liquid substances. The recent determinations of "b" of water by L. Gay[1] are as follows:

Temperature (abs.)	Mol. vol. in cc.	b in cc.
323	18.233	14.577
343	18.424	14.928

According to the theory of van der Waals, "b" is four times the actual volume, but recently T. W. Richards[2] has shown that it is nearly equal to it. If we admit the analogy between the gaseous state and solution, we must yet acknowledge that there is a very small free volume in solution in comparison with its total volume, for the free movement of the solute molecules by their kinetic energy. And this fact always holds, even when the solution is *very dilute*. In other words, we can not neglect the actual volume of the solvent in any dilution in the determination of the condition of the solution.

If, therefore, the analogy between the gaseous state and solution holds, the equation of the state of solution is not van't Hoff's equation:

$$PV = nRT$$

but

$$P(V-b') = nRT^*$$

where "b'" is not the same as "b" for the pure solvent, but near it and it cannot to be neglected in connection with V. Yet, the van't Hoff's equation holds in dilute solution and then its coincidence with the gas law may be accidental. Thus the analogy, which had been suggested as a plausible explanation by van't Hoff, now becomes questionable.

On the other hand, chemists who treat the problems of solution thermodynamically, have explained the osmotic relations of solution with the difference of activities or free energies between solution and solvent, quite indifferently to the hypothesis of the cause of osmotic

1 C. R., **157**, 711, 1914, and **158**, 34 (1914).

2 J. Amer. chem. soc., **36**, 2417 (1914).

* Very similar equation for the osmotic pressure has been proposed by O. Sackur (Zs. physik. Chem., **70**, 477. 1910) such as, $P(V-b)=RT$, where P is the osmotic pressure, V the volume in which 1 mol of solute is dissolved. This equation shows fairly good coincidence with the experimental data even in quite concentrated solutions, but as seen from the definition of V in this equation it is not the same as the above derived equaiton, and moreover the Sackur's equation does not support the analogy of the gaseous state and solution.

pressure. In the recent work of E. W. Washburn[1]: "An Introduction to the Principles of Physical Chemistry" the definition of osmotic pressure is clearly given as follows: "The osmotic pressure of a solution is the pressure difference which must be established upon the solution and pure solvent respectively, in order to make the escaping tendency of the solvent the same from both of them. The osmotic pressure is, therefore, not a real pressure existing within the solution but is a definite physical quantity quite independent of osmosis, semipermeable membrane or molecular theory. It is connected with the other colligative properties of the solution by definite relation which can be deduced by purely thermodynamic reasoning. For dilute solutions the osmotic pressure becomes in the limit equal to CRT where C is the concentration of solute, but as the concentration increases the osmotic pressure approaches infinitely as its upper limit."

In argument such thermodynamical theories, Findlay[2] says as follows: "Valuable as the thermodynamical theory of solutions has proved to be in correlating quantitatively the properties of solutions, it throws but little light on the mechanism of osmosis or on the intimate structure and constitution of solutions. Nor has it ever claimed to do so. Thermodynamics gives us a theory of *solutions*; it gives us no theory of *solution*."

Of course, we can not content ourselves with merely purely thermodynamieal deductions for an explanation of the osmotic phenomena, or for a theory of solution, and we need to explain this phenomena from two sides, that is, qualitative and quantitative. Once more let us quote Findlay's words: "For it must be remembered that the problem of solutions consists of two parts, the qualitative and quantitative. On the one hand, insight is desired into the nature and constitution of solution, into the processes involved in the production of a solution whether these depend on chemical affinity, surface tention, or other causes; and, on the other hand, an equal need is felt for a some quantitative expression by means of which the relationships between the concentration of solutions and their physical properties can be studied quantitatively and computed. The qualitative and quantitative are, however, but two complementary sides of one problem and while some investigators may attach surpreme importance to the qualitative side—to the construction of pictures or models of the con-

1 *See* p. 161.

2 Osmotic Pressure, p. 47.

stitution of solutions—others will make more use of the quantitative relationships by means of which the efficiency of these models can be tested. It is, however, by mutual understanding and co-operation be-between the workers on the two sides, that knowing will finally be attained."

Against the osmotic theory of solution of van't Hoff, the criticism has been levelled from the time of its enunciation to the present day, by L. Meyer[1], Quincke[2], Kahlenbeg[3] and more recently in the controversy between van Laar and Ehrenfest[4]. In the opinion of Ehrenfest, the osmotic pressure is not caused by the bombardment on a semipermeable membrane of the molecules of the solute, as has just been described, but this is caused by the water which penetrate through the semipermeable membrane, giving rise to a hydrostatic pressure which prevent the further intrussion of the water. Thus, there are many theories opposing the osmotic theory of van't Hoff, yet none are satisfactory on both sides, qualitative and quantitative.

If van't Hoff's theory as to the cause of osmotic pressure is rejected, its place would be taken by that of osmotic suction as proposed by Ehrenfest. The writer has held that opinion from the beginning of this study of solution, but has not published it until now.

In the preceding report, on the investigation, of the change of molecular solution volumes of solute and solvent in solution, a hypothetical picture of solution was attained and according to it the author tried to explain the osmotic pressure qualitatively and quantatively in the following way.

As described in the preceding paper, in the solution of *nonvolatile substance*, the molecular solution volume of solute increases with the increase of concentration of solute; and on the contrary the molecular solution volume decreases: this phenomenon makes the supposition plausible that the molecules of solute and solvent will compress each other by their cohesion or physico-chemical affinity in solution. This compressed state may perhaps be comparable to the state of stress and strain, and the effect of pressure does not, therefore, express itself as an external pressure. The order of this pressure can be estimated, as

1 Zs. physik. chem., **5**, 23 (1890).
2 Ann. Physik, (iv) **7**, 681 (1902).
3 J. Phys. chem., **10**, 141 (1906).
4 Nature, **97**. 68 (1916).

described in the preceding paper, in comparision with the external pressure which would be needed to compress the solvent only.

It is not the only possible supposition that there exists a parallelism between the change of "molecular solution volumes" of solute and solvent and that of their molecular volumes in solution. The phenomenon of the change of molecular solution volumes may, however, be explained in another way. In solution, some molecules of solute and solvent will perhaps not be homogeneously disintegrated but in polymerised state or in some states of aggregation and only those which are disintegrated approach one another and are compressed in their volumes by the mutual affinity or they build up some kinds of solvate. Admitting such a state of solution, the observed phenomenon of the change of molecular solution volumes may be explained by the change of the degree of disintegration of molecules caused by the change of the concentration of solution.

In any supposition whatever, the mean molecular volumes of solute and solvent in solution will be smaller than those in pure state.

Now, admitting the state of solution to be of such a nature, let a pure solvent be brought into contact with a solution by a semi-permeable membrane, then it will penetrate into the solution to lower the compression of the solvent molecules in solution: on the contrary, if the pure solute be brought in contact with solution it will dissolve until it saturates the solution, to decrease the compression of the solute molecules in solution. The relation of the molecular solution volume of solute in the saturated solution and its solubility have already been considered in the preceding paper. In solution, solute and solvent are only relative term; and from this point of view, *the osmotic pressure can be explained as the solutional pressure of the water into solution.*

According to this, the osmotic pressure is the pressure which comes into play against the penetration of the solvent into the solution; and the cause of hydrostatic pressure thus produced in solution is the penetration of a quantity of solvent into the solution. Then inner pressure of compression of the solvent in solution is, therefore, *the first cause of the osmotic pressure.*

In concentrated solution, its inner pressure would not be equal to the osmotic pressure or hydrostatic pressure produced in solution, but in dilute solution, these pressures would be equal. The numerical value of inner pressure in dilute solution can not be determined exactly, but it seems to be of the order of the osmotic pressure as described in the preceding paper. This is the author's theory of the osmotic pressure in the qualitative side; and it is something new in its explanation why hydrostatic pressure would be produced in the side of the solution which is in contact with the pure solute.

Further, as to the quantitative side of this theory of osmotic pressure, reference must be made to Porter's very comprehensive theory of compressible solutions of any degree of concentration[1]. Porter's attention was at first directed to the success of the direct determination of the osmotic pressure by Earl of Berkeley and E. G. Hartley[2]. Their method of measurement was to determine the equilibrium pressure, that is the pressure which must be supplied to the solution to bring about a state of equilibrium between it and the solvent so that no solute, i.e. water, passes in another direction as a whole when the solution and solvent are separated by a semipermeable membrane, Porter studied the relation between osmotic and vapour pressure purely thermodynamically and derived the following equation:

$$\int_{A+\pi_{a\pi}}^{A+p} s\,dp = \int_{\pi_{a\pi}}^{\pi_{a0}} v\,dp + \int_{A+\pi_{a0}}^{A+p_0} u\,dp.$$

In this equation s denotes the diminution in volume when 1 gram of solvent escapes from a practically infinite volume of solution, v is the specific volume of the vapour, and u is the specific volume of solvent; A is the atmospheric pressure; π_{a0} is the vapour pressure of the solvent in air when it is under a total pressure of $A+\pi_{a0}$; and $\pi_{a\pi}$ is the vapour pressure of the solution in air when it is under a total pressure of $A+\pi_{a\pi}$.

One of the most important conclusions from this equation is that when a solution is in osmotic equilibrium with the pure solvent, the vapour pressure of the solution is equal to the vapour pressure of the pure solvent, each measured for the actual hydrostatic pressure of the fluid to which it refers.

Now, returning to the author's consideration of osmotic pressure, the solution, which is in osmotic equilibrium with pure solvent through a semipermeable membrane, would have a hydrostatic pressure caused by the penetration of the pure solvent and this hydrostatic pressure is acting to prevent the further penetration of the solvent. In the opinion of the writer, this cause of the penetration of solvent into solution is the compression of the solvent molecules in the solution. And compression or inner pressure in solution would be directly compared to

1 Proc. R. Soc., London, **76** A, 519. (1907) and **80** A, 457. (1908) Porter's theory is fully quoted in the recent work W. C. McC. Lewis: A system of Physical Chemistry (1916) p. 224.

2 Phil. Trans, A, **206**, 486. (1906).

the hydrostatic pressure produced in solution or *the external pressure added on the solution to establish the osmotic equilibrium with the pure solvent* as Berkley and Hartly[1] did. From this point of view the osmotic pressure is replaced by an external pressure added on the solution, and the relation of osmotic pressure to other properties of solution, such as vapour pressure, may easily be drawn.

The relation of the vapour pressure of a liquid and its external pressure is represented by the well known relation of Poynting:

$$\left(\frac{\partial p}{\partial P}\right)_T = \frac{V}{v}, \qquad (1)$$

where P and p are the external pressure on a liquid and its vapour pressure respectively, V and v are molecular volumes in liquid and vapour states respectively.

According to the Porter's theory, the solution, which is in osmotic equilibrium with the pure solvent, has the same vapour pressure as that of the pure solvent and when the external pressure added on the solution is removed, its vapour pressure will be lowered, and its lowering may be estimated from Poynting's equation applying it directly on solution where P, the external pressure added on the solution, denotes the osmotic pressure of the solution. But, upon the older view of osmotic pressure, the osmotic pressure is considered to exist even when the solution stands alone without any contact with the pure solvent. To represent such osmotic pressure or inner pressure of the author, P in the above equation must change its sign, then the equation becomes as follows:

$$\left(\frac{\partial p}{\partial P}\right)_T = -\frac{V}{v}, \qquad (2)$$

where P denotes the osmotic pressure or the author's inner pressure.

"It is a well known experimental fact that if we add, say an inert gas, to a vessel containing a liquid and its saturated vapour, that increases in pressure in the vessel due to the inert gas, causes an increase in the actual pressure (partial pressure) of the saturated vapour. From the molecular stand point one might regard the phenomenon as to the closer packing of the molecules of liquid under the increased pressure, and therefore the possibility exists of more molecules per unit surface area capable of forming vapour, i.e. the vapour pressure rises."[2] This relation is mathematically shown in Poynting's equation. In the author's view, the molecules of the solvent in solution are compressed by the inner pressure, yet the vapour pressure of the solvent is depressed, apparently in contradiction to

1 *Loc. cit.*

2 *From* W. C. McC. Lewis: A System of Physical Chemistry, Vol. II, p. 224.

the above reasoning. But this may be easily explained in the following way. When the volume change accompanying the formation of the solution is neglected, the number of molecules of the solvent on unit surface of a solution are not increased by compression of the solvent or increase of the inner pressure, and on the contrary, the contact surface of the solvent molecules with the vapour phase decreases by the insertion of the solute molecules; thus the vapour pressure of a solution would be depressed. As to the mathematical relation of this lowering, it is expressed by the above eq. (2) which is of the same form as Poynting's equation.

Having got eq. (2), relating to the osmotic pressure, we can easily get the relations of the colligative properties of solution and the osmotic pressure as E. W. Washburn has comprehensively described in "A Simple System of Thermodynamic Chemistry based upon a Modification of the Method of Carnot."[1]

Now, the derivation of the van't Hoff's osmotic equation from eq. (2) may be described as follows. If V_0 be the molecular volume of a pure solvent under one atmosphere pressure, then V, the molecular volume of the solvent under the external pressure of one atmosphere plus inner pressure P, is

$$V = V_0(1-\alpha P),$$

where α is compressibility of the solvent. Assuming that the vapour of this solvent obeys the gas law, or that $pv=RT$ holds for it, and putting these relations in eq. (2), we obtain the following expression :

$$RTd\ln p = -V_0(1-\alpha P)dP,$$

Integrating this equation, we have

$$RT\ln p = -V_0(P-\frac{1}{2}\alpha P^2)+RT\ln p_0,$$

or

$$P-\frac{1}{2}\alpha P^2 = -\frac{RT}{V_0}\ln\frac{p}{p_0}, \qquad (3)$$

where p_0 is the vapour pressure of the pure solvent under one atmosphere pressure. Neglecting the second term $\frac{1}{2}\alpha P^2$ against P, by the reason of the very small value of α, and expanding eq. (3), we have

$$P = \frac{RT}{V_0}\left[\left(\frac{p_0-p}{p_0}\right)+\frac{1}{2}\left(\frac{p_0-p}{p_0}\right)^2+\frac{1}{3}\left(\frac{p_0-p}{p_0}\right)^3\cdots\cdots\right]. \qquad (4)$$

In dilute solutions, we may take the first term only, that is

$$P = \frac{RT}{V_0}\frac{p_0-p}{p}. \qquad (5)$$

1 J. Amer. Chem. Soc., **32**, 653. (1910).

This expression is nothing but the van't Hoff's equation. But to get the equation $PV=nRT$, we must combine eq. (5) with Raoult's equation

$$\frac{p_0-p}{p}=\frac{n}{N+n}. \qquad (6)$$

Purely thermodynamically, without using the idea of osmotic pressure, we can not deduce Raoult's equation directly. Thermodynamics gives us only Duhem-Margules's differential equation about the relations of vapour pressures of a solution, such as

$$x\frac{\partial \ln p_1}{\partial x}+(1-x)\frac{\partial \ln p_2}{\partial x}=0, \qquad (7)$$

where $x=\frac{N_1}{N_1+N_2}$, $1-x=\frac{N_2}{N_1+N_2}$ and N_1, N_2 and p_1, p_2 are the numbers of mols and partial pressures of components of a solution respectively. As a special solution of this equation, Dolezalek[1] proposed the following equations :

$$p_1=p_{0,1}\frac{N_1}{N_1+N_2}, \quad p_2=p_{0,2}\frac{N_2}{N_1+N_2},$$

where $p_{0,1}$ and $p_{0,2}$ are the vapour pressures of components in pure state. Raoult's equation is a special case of Dolezalek's solution where the solution is dilute and one component is nonvolatile.

Now, recognizing Raoult's equation we can easily get from eq. (5) the following relation,

$$P=\frac{RT}{V_0}\frac{n}{N+n},$$

or

$$PV=nRT. \qquad (8)$$

One must notice that on the derivation of this equation the gas constant R comes from the solvent part not from the solute part as in the case of the van't Hoff's equation.

In conclusion, to sum up briefly the contents of this treatise. The analogy of the gaseous state and solution is questionable, and the coincidence of the equations of these states may perhaps be accidental. If one assume the above analogy, it does not lead to the van't Hoff's equation, as the equation of the state of solution, but another. The

1 Zs. physik. Chem., **64**, 727, (1908).

author holds the same view as Ehrenfest with respect to osmotic pressure, and has further explained the cause of the penetration of the pure solvent into the solution to cause the osmotic pressure. From his view of the explanation of osmotic pressure, the mathematical expression of the state of solution can easily be derived.

Cordial thanks are due to Prof. Osaka. for interest taken in this work.

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